<table>
<thead>
<tr>
<th>PROBLEM 1</th>
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| **PROBLEM 1**
Assuming that the molecular ion is the base peak (100% abundance) what peaks would appear in the mass spectrum of each of these molecules:
(a) C₂H₅BrO
(b) C₆₀
(c) C₆H₄BrCl
In cases (a) and (c) suggest a possible structure of the molecule. What is (b)? |

**Purpose of the problem**
To give you some practice with mass spectra and, in particular, at interpreting isotopic peaks. The molecular ion is the most important ion in the spectrum and often the only one that interests us.

**Suggested solution**
Bromine has two isotopes, ⁷⁹Br and ⁸¹Br in about a 1:1 ratio. Chlorine has two isotopes ³⁵Cl and ³⁷Cl in about a 3:1 ratio. There is about 1.1% ¹³C in normal compounds.

(a) C₂H₅BrO will have two main molecular ions at 124 and 126. There will be very small (2.2%) peaks at 125 and 126 from the 1.1% of ¹³C at each carbon atom.

(b) C₆₀ has a molecular ion at 720 with a strong peak at 721 of 60 x 1.1 = 66%, more than half as strong as the ¹²C peak at 720. This compound is buckminsterfullerene.

(c) This compound is more complicated. It will have a 1:1 ratio of ⁷⁹Br and ⁸¹Br and a 3:1 ratio of ³⁵Cl and ³⁷Cl in the molecular ion. There are four peaks from these isotopes (ratios in brackets) C₆H₄⁷⁹Br³⁵Cl (3), C₆H₄⁸¹Br³⁵Cl (3), C₆H₄⁷⁹Br³⁷Cl (1), and C₆H₄⁸¹Br³⁷Cl (1), the masses of these peaks being 190, 192, 192, and 194. So the complete molecular ion will have three main peaks at 190, 192, and 194 in a ratio of 3:4:1 with peaks at 191, 193, and 194 at 6.6% of the peak before it.

Compounds (a) and (c) might be isomers of compounds such as these:

![Br₃OH, Cl₃Br, Cl₃Br, Br₃Cl]  | Buckminsterfullerene is on page 25 of the textbook.
**PROBLEM 2**

Ethyl benzoate $\text{PhCO}_2\text{Et}$ has these peaks in its $^{13}\text{C}$ NMR spectrum: 17.3, 61.1, 100-150 (four peaks) and 166.8 ppm. Which peak belongs to which carbon atom? You are advised to make a good drawing of the molecule before you answer.

**Purpose of the problem**

To familiarize you with the four regions of the spectrum.

**Suggested solution**

It isn’t possible to say which aromatic carbon is which and it doesn’t matter. The rest are straightforward.

![Diagram of ethyl benzoate](image)

**PROBLEM 3**

Methoxatin was mentioned on page 44 of the textbook where we said 'it proved exceptionally difficult to solve the structure by NMR.' Why is it so difficult? Could anything be gained from the $^{13}\text{C}$ or $^1\text{H}$ NMR? What information could be gained from the mass spectrum and the infra red?

**Purpose of the problem**

To convince you that this structure really needs an X-ray solution but also to get you to think about what information is available by the other methods. Certainly mass spectroscopy, NMR, and IR would have been tried first.

**Suggested solution**

There are only two hydrogens on carbon atoms and they are both on aromatic rings. There are only two types of carbon atom: carbonyl groups and unsaturated ring atoms. This information is mildly interesting but is essentially negative—it tells us what is not there but gives us no information on the basic skeleton, where the carboxylic acids are, nor does it reveal the 1,2-diketone in the middle ring.
The mass spectrum would at least give the molecular formula C_{14}H_{6}N_{2}O_{8} and the infra-red would reveal an N–H group, carboxylic acids, and perhaps the 1,2-diketone. The X-ray was utterly convincing and the molecule has now been synthesised, confirming the structure.

PROBLEM 4

The solvent formerly used in some correcting fluids is a single compound C_{2}H_{3}Cl_{3}, having 13C NMR peaks at 45.1 and 95.0 ppm. What is its structure? How would you confirm it spectroscopically? A commercial paint thinner gives two spots on chromatography and has 13C NMR peaks at 7.0, 27.5, 35.2, 45.3, 95.6, and 206.3 ppm. Suggest what compounds might be used in this thinner.

Purpose of the problem

To start you on the road to structure identification with one very simple problem and some deductive reasoning. It is necessary to think about the size of the chemical shifts to solve this problem.

Suggested solution

With the very small molecule C_{2}H_{3}Cl_{3} it is best to start by drawing all the possible structures. In fact there are only two.

The first would have a peak for the methyl group in the 0-50 region and one for the CCl_{3} group at a very large chemical shift because of the three chlorine atoms. The second isomer would have two peaks in the 50-100 region, not that far apart. The second structure looks better but it would be easily confirmed by proton NMR as the first structure would have one peak only but the second would have two peaks for different CHs. The solvent is indeed the second structure 1,1,2-trichloroethane.
Two of the peaks (45.3 and 95.6) in the paint thinner are much the same as those for this compound (chemical shifts change slightly in a mixture as the two compounds dissolve each other). The other compound has a carbonyl group at 206.3 and three saturated carbon atoms, two close to the carbonyl group (larger shifts) and one further away. Butanone fits the bill perfectly. You were not expected to decide which CH₂ group belongs to which molecule—that can be found out by running a spectrum of pure butanone.

![Butanone spectrum](image)

**Problem 5**

The ‘normal’ O–H stretch in the infrared (i.e. without hydrogen bonding) comes at about 3600 cm⁻¹. What is the reduced mass (μ) for O–H? What happens to the reduced mass when you double the mass of each atom in turn, i.e. what is μ for O–D and what is μ for S–H? In fact, both O–D and S–H stretches come at about 2,500 cm⁻¹. Why?

**Purpose of the problem**

To get you thinking about the positions of IR bands in terms of the two main influences: reduced mass and bond strength.

**Suggested solution**

Using the equation on page 64 of the textbook we find that the reduced mass of OH is 16/17 or about 0.94. When you double the mass of H, the reduced mass of OD becomes 32/18 or about 1.78 – nearly double that of OH. But when you double the mass of O, the reduced mass of SH is 32/33 or about 0.97 – hardly changed from OH! The change in the reduced mass from OH to OD is enough to account for the change in stretching frequency – a change of about √2. But the change in reduced mass from OH to SH cannot account for the change in frequency. The explanation is that the S–H bond is weaker than the O–H bond by a factor of about 2. So both both O–D and S–H absorb at about the same frequency.

There is an important principle to be deduced from this problem. Very roughly, all the reduced masses of all bonds involving the heavier elements (C, N, O, S etc) differ by relatively small amounts and the differences in stretching frequency are mainly due to changes in bond strength, though it can be significant in comparing, say, C–O with C–Cl.
With bonds involving hydrogen does the reduced mass becomes by far the important factor.

**PROBLEM 6**

Three compounds, each having the formula C₃H₅NO, have the IR data summarized here. What are their structures? Without $^{13}$C NMR data it might be easier to draw some or all possible structures before trying to decide which is which. In what ways would $^{13}$C NMR data help?

(a) One sharp band above 3000 cm⁻¹ and one strong band at about 1700 cm⁻¹

(b) Two sharp bands above 3000 cm⁻¹ and two bands between 1600 and 1700 cm⁻¹

(c) One strong broad band above 3000 cm⁻¹ and a band at about 2200 cm⁻¹

**Purpose of the problem**

To show that IR alone does have some use but that NMR data are usually essential as well. In answers to exam questions of this type it is important to show how you interpret the data as well as to give a structure. If you get the structure right, this doesn’t matter, but if you get it wrong, you may still get credit for your interpretation.

**Suggested solution**

(a) One sharp band above 3000 cm⁻¹ must be an N–H and one strong band at about 1700 cm⁻¹ must be a carbonyl group. That leaves C₂H₄, so we might have one of the structures shown below, though other less likely structures are possible too. $^{13}$C NMR data would help as it would definitely two types of saturated carbon (along with the carbonyl group) for the first compound, but only one for the second.

(b) Two sharp bands above 3000 cm⁻¹ must be an NH₂ group and two bands between 1600 and 1700 cm⁻¹ suggest a carbonyl group and an alkene. This leaves us with three hydrogen atoms so we must have something like the molecules below. $^{13}$C NMR data would help as it would show an alkene carbon shifted downfield by being joined to electronegative nitrogen in the second case.

■ You will meet other ways of distinguishing these compounds in chapters 13 and 18.
(c) One strong broad band above 3000 cm\(^{-1}\) must be an OH group and a band at about 2200 cm\(^{-1}\) must be a triple bond, presumably CN as otherwise we have nowhere to put the nitrogen atom. This means structures of this sort.

**PROBLEM 7**

Four compounds having the formula C\(_4\)H\(_6\)O\(_2\) have the IR and NMR data given below. How many DBEs (double bond equivalents—see p. 75 in the textbook) are there in C\(_4\)H\(_6\)O\(_2\)? What are the structures of the four compounds? You might again find it useful to draw a few structures to start with.

(a) IR: 1745 cm\(^{-1}\); \(^{13}\)C NMR 214, 82, 58, and 41 ppm
(b) IR: 3300 cm\(^{-1}\) (broad); \(^{13}\)C NMR 62 and 79 ppm.
(c) IR: 1770 cm\(^{-1}\); \(^{13}\)C NMR 178, 86, 40, and 27 ppm.
(d) IR: 1720 and 1650 cm\(^{-1}\) (strong); \(^{13}\)C NMR 165, 133, 131, and 54 ppm.

**Purpose of the problem**

First steps in identifying compound from two sets of data. Because the molecules are so small (only four carbon atoms) drawing out a few trial structures is a good way to start.

**Suggested solution**

Here are some possible structures for C\(_4\)H\(_6\)O\(_2\). It is clear that there are two double bond equivalents and that double bonds and rings are likely to feature. Functional groups are likely to include alcohol, aldehyde, ketone and carboxylic acid.

(a) IR: 1745 cm\(^{-1}\) must be a carbonyl group; \(^{13}\)C NMR 214 must be an aldehyde or ketone, 82 and 58 look like two carbons next to oxygen and 41 is a carbon not next to oxygen but not far away. As the second
oxygen doesn't show up in the IR, it must be an ether. As there is only one double bond, the compound must be cyclic. The suggests just one structure.

(b) IR: 3300 cm⁻¹ (broad) must be an OH; ¹³C NMR 62 and 79 show a symmetrical molecule and no C=O so it must have a triple bond and a saturated carbon next to oxygen. This again gives only one structure.

(c) IR: 1770 cm⁻¹ must be some sort of carbonyl group; ¹³C NMR 178 suggests an acid derivative, 86 is a saturated carbon next to oxygen, 40 and 27 are saturated carbons not next to oxygen. There is only one double bond so it must be a ring. Looks like a close relative of (a).

(d) IR 1720 and 1650 cm⁻¹ (strong) must be C=C and C=O; ¹³C NMR 165 is an acid derivative, 131 and 133 must be an alkene, and 54 is a saturated carbon next to oxygen. That defines all the carbon atoms. It is not significant that we cannot say which alkene carbon is which.

![Chemical structures](image)

**PROBLEM 8**

You have dissolved tert-butanol in MeCN with an acid catalyst, left the solution overnight, and found crystals in the morning with the following characteristics. What are the crystals?

![Reaction Scheme](image)

IR: 3435 and 1686 cm⁻¹; ¹³C NMR: 169, 50, 29, and 25 ppm. Mass spectrum (%): 115 (7), 100 (10), 64 (5), 60 (21), 59 (17), 58 (100), and 56 (7). Don't try to assign all the peaks in the mass spectrum.

**Purpose of the problem**

This is a common situation: you carry out a reaction and find a product that is not starting material, but what is it? You'll need to use all the information and some logic. What you must not do is to decide in advance what the product is from your (limited) knowledge of chemistry and make the data fit.

**Suggested solution**

The molecular ion in the mass spectrum is 115 and is presumably C₆H₁₃NO – the sum of the two reagents t-BuOH and MeCN. It appears
that they have added together but the IR shows that neither OH nor CN has survived. So what do we know?
- The IR tells us we have an N-H and a C=O group, accounting for both heteroatoms.
- The NMR shows a carbonyl group (169) and three types of saturated carbon. There must be a lot of symmetry, suggesting that the t-Bu group has survived. This leaves four fragments: NH, C=O, Me, and t-Bu. We can join these up in two ways:

We might prefer the second as it retains the skeleton of MeCN, but a better reason is the base (100%) peak in the mass spectrum at 58. This is Me₂C-NH₂⁺ which could easily come from the second structure but only by extensive reorganisation of the first structure. The second structure is in fact correct but we need proton NMR (chapter 13) to be sure.

**PROBLEM 9**

How many signals would you expect in the ¹³C NMR spectrum of these compounds?

**Purpose of the problem**

To get you thinking about symmetry.

**Suggested solution**

Compound A has tetrahedral symmetry and there are only two types of carbon: every CH₂ is the same, as is every CH, so it has two signals. This is the famous compound adamantane – a crystalline solid in spite of its
being a hydrocarbon with only ten carbon atoms. If you do not see the
symmetry, make a model – it is a beautiful structure.

Compound B is symmetrical too: the two C=O groups are the same
and so are all the other carbon atoms in the ring. It is an orange
crystalline solid called quinone. Two signals.

Compound C is naphthalene and has high symmetry: the two benzene
rings are the same and there are only three types of carbon atom.
Three signals.

Compound D is ‘triethanolamine’ used a lot by biochemists. It has
threefold symmetry and only two types of carbon atom. Two signals.

Compound E is ‘EDTA’ (ethylenediaminetetraacetic acid) an
important chelating agent for metals. This time there are three types of
carbon atom. Three signals.